



Pretreatment of agricultural residues for co-gasification via torrefaction

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ABSTRACT

Torrefaction is a main pretreatment technology for improving the properties of agricultural biomass in order to deal with such problems as high bulk volume, high moisture content and poor grindability. Two typical agricultural residues, rice straw and rape stalk were torrefied in a vertical reactor at 200 °C, 250 °C and 300 °C for 30 min, under inert atmosphere. The product distribution profiles of solid, liquid and gases were obtained. The grindability of the torrefied biomass was evaluated by the particle size distribution after being milled in a ball mill. It was found that temperature strongly affected the torrefied biomass and the type of feedstock influenced the conversion rate due to the different volatile content in raw biomass. An increase of torrefaction temperature leads to a decrease in solid bio-char yield and an increasing yield in the volatile matters including liquid and non-condensable gases. The maximum increase of the heating value of the torrefied residue compared with the raw material is 17% for the rice straw and 15% for the rape stalk, respectively. On the other hand, the torrefied residues are liable to be pulverized. A kinetic study on the generation of main non-condensable gases was accomplished, which shows that the gases are formed through parallel independent first-order reactions. The kinetic characteristic parameters for the generation of each gas were determined. A novel method which combined torrefaction with co-gasification to improve the efficiency of biomass utilization is promising.

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1. Introduction

Agricultural residues are biomass resources with negligible sulfur and nitrogen, and more importantly they are CO₂ neutral. The biomass such as straw, firewood, and various kinds of organic wastes, accounts for 72.2% of total biomass energy resources in China. It was reported that the total output of crop straw was up to 622 million ton in 2002 [1]. However, the ratio of biomass being utilized as energy was approximately 3% [2]. Most of the biomass is wasted by corrosion or combustion on farmland. The efficient utilization of agricultural residue to supply energy becomes more urgent than ever because of a shortage of fossil fuel and environmental problems caused by energy consumption. The thermo-chemical conversions for biomass involve combustion, pyrolysis, gasification and liquefaction [3–5]. However, there are many barriers in direct utilization of the agricultural residues in energy supply owing to the characteristics of the biomass. The high moisture content and low calorific value of biomass influence the efficiency of combustion and pyrolysis [4]. The lignocellulosic materials with fibrous structure are difficult to grind where fine particles are needed during gasification in entrained flow gasifier or co-firing with pulverized coal [6]. How to deal with the tar yielded during the low temperature gasification and pyrolysis of biomass is still a bottleneck of the technology nowadays.

Moreover, the agricultural residues have large bulk volume and usually are scattered on a large scale, which greatly increases the cost of logistics operations [7]. The seasonable availability also limits the biomass exploitation in high efficient reactors which need a great deal of feedstock.

The pretreatment technology can improve the efficiency of biomass utilization or lead to a reduction of the cost of the transport and storage of biomass. Researchers have paid more and more attention to the pretreatment technologies, especially those of thermal chemical conversion methods, to upgrade the biomass (woody and herbaceous) properties. The main purposes are either for transforming biomass to convenient energy of bio-oil or increasing the energy density via pre-pyrolysis to obtain solid bio-char. The former is flash pyrolysis carried out at high heating rate and relatively higher temperature with a short residence time of several seconds [8–11]. However, the latter is a mild pyrolysis process called torrefaction or carbonization (wood) [6,11–16]. Torrefaction is performed under approximately atmospheric pressure at relatively low heating rate of less than 50 °C min^{−1}. Temperatures vary from 200 °C to 300 °C according to the types of biomass. With the absence of oxygen, the biomass is partly decomposed and yields a uniform solid product with very low moisture content and high calorific value, condensable liquid and non-condensable gases.

The main advantages of torrefied biomass are:

(a) Hydrophobic solid product with higher calorific value [6].

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- (b) Greatly enhanced grindability, since the energy consumption for milling is three to seven times lower than that of raw materials [6,16].
- (c) High porosity, greater reactivity during combustion and gasification [16,17].

Currently, plenty of data about woody biomass torrefaction is available. Most research has focused on the compositional changes of biomass by proximate and ultimate analysis, along with the products distribution [18–20]. Some studies have investigated the composition of liquid and gas phase released during pyrolysis [21,22]. Torrefied wood powder can be an option for co-firing or co-gasification [11,13]. The previous work suggested that torrefied biomass is a suitable feedstock for entrained flow gasification, the systems previously not considered feasible for raw biomass fuels. Prins [16] came to a conclusion by modeling evaluation that the oxygen-blow entrained flow gasification of torrefied wood seemed to be an attractive option to conserve the chemical exergy of wood maximally in the gas product, at a high gasification temperature.

However, less attention has been paid to the torrefaction of agricultural biomass. More research is required to understand the chemical and physical processes in torrefaction of agricultural residues. In this study, the torrefaction behaviors of two agricultural residues from eastern China, rice straw and rape stalk, were investigated. The focus of the work is on the temperature dependence of the product yields and gas composition. Meanwhile, the changes in the grindability of the torrefied biomass were evaluated. The experiments were carried out between 200 °C and 300 °C in a vertical reactor under inert atmosphere. Torrefied biomass was ground in a ball mill and then sieved to determine the particle size distribution. Finally, a process combining torrefaction with co-gasification is proposed because volatiles can be exploited for autothermal operation of the torrefaction.

2. Experimental

2.1. Materials

Two typical agricultural residues, rice straw and rape stalk, from Anhui Province in eastern China, were cut into slices of an average length of 25 mm. The diameter of the original biomasses is about 2 mm. The residues were dried for 24 h at 95 °C before the experiments. Some studies [5] showed that particle sizes below 5 mm did not exert any influence on the pyrolysis process rate. Table 1 shows the proximate and ultimate analysis of the residues (air dry basis).

Table 1
Proximate and ultimate analysis of the rice straw and rape stalk (air dry basis).

Samples	Proximate analysis (wt%)					Ultimate analysis (wt%)			
	Moisture	Volatile matter	Fixed carbon	Ash	HHV (MJ kg ⁻¹)	C	H	O	N
Rice straw	5.12	68.83	17.46	8.59	17.12	39.00	5.08	40.96	1.03
Rape stalk	1.19	76.35	19.30	3.16	18.75	46.96	6.13	41.95	0.37

Table 2
Influence of temperatures on the yields of torrefied samples and heating value.

Samples	Temperature (°C)	Solids (wt%)	Liquids (wt%)	Gases (wt%)	Conversion (wt%)	HHV (MJ kg ⁻¹)
Rice straw	200	59.84	3.47	36.69	40.16	17.16
	250	40.32	4.23	55.45	59.68	18.03
	300	36.57	6.56	56.87	63.43	18.68
Rape stalk	200	63.29	6.76	29.95	36.71	19.50
	250	38.26	9.42	52.32	61.74	20.10
	300	25.30	10.04	64.66	74.70	21.59

2.2. Torrefaction and pulverization

A vertical reactor used for the torrefaction is a corundum tube with a diameter of 60 mm and a length of 500 mm. A distributor plate is located 200 mm above the bottom. In each case a biomass sample of 15 ± 0.1 g was heated with a nitrogen flow rate of 500 ml min⁻¹ at three different final temperatures (200 °C, 250 °C, and 300 °C). The pressure in the system maintains about 1.96 kPa. Previous experiments showed that the inert gas flow rate did not influence the process rate. The heating rate was set about 30–45 °C min⁻¹ since this condition did hardly influence the products during biomass slow pyrolysis [23–25]. After 30 min, heating was turned off and then opened another nitrogen flow to make the furnace cooling down soon. Nitrogen as a sweep gas was heated at the entrance of the tube and then carried the pyrolysis products out of the reactor. The products were removed from the hot zone to minimize the second reactions between the liquid and the char, and to maximize the solid yield. A two-necked flask immersed in liquid nitrogen was used as a trapping system for condensable liquid. Non-condensable gases went through a filter to remove the carbon soot before entering an infrared gas analysis (Gasboard-5110, Wuhan, China). The lowest limit of concentration is above 0.001% by volume. The gas composition and concentration were recorded continuously throughout the heating process. Finally, the weight of the bio-char and the amount of the liquids obtained were measured. A bomb calorimeter (XRY-1C, Shanghai, China) was applied to analyze the heating value of the torrefied samples. Thus the data can be used to evaluate the energy yield.

In order to investigate the grindability of the torrefied rice straw and rape stalk, the samples were ground in a ball mill for 1 min. As comparison, an original sample with the same weight is treated by the same method. The powder samples were then sieved into four size fractions including greater than 450 μm, 450–150 μm, 150–100 μm and less than 100 μm. The particle size distribution is evaluated by the weight percentages of each fraction.

3. Results and discussion

3.1. Yields of torrefied products

The thermal decomposition of the agricultural residues under torrefaction temperatures produces mainly three products: a solid product which retains 30–66% of the energy content of the feedstock, a condensable liquid including most of moisture, acetic acid and other oxygenates and non-condensable gases (mainly carbon dioxide, carbon monoxide and small amounts of methane). The last two products can be represented by volatiles. The total

yield of volatiles increases with both raising reaction temperature and higher volatile content. Table 2 gives the data of solid, liquid and gas yields of the two residues during torrefaction at different temperatures. As the temperature increases, the yield of solid product decreases, whereas the yield of liquid and gas increases accordingly. That is a result of the competition between charring and devolatilization reactions which are more reactive at higher temperature. The bio-char yield of the rice straw decreases roughly by 23 wt% when the torrefaction temperature increases from 200 °C to 300 °C and a larger decrease of 38 wt% is observed for the rape stalk. The particles tended to shrink in all directions and the fiber linking between particles disappeared. [6] Thus the biomass particles became more spherical which can improve the poor flow properties of the biomass. Furthermore, the reduced size led to a greater bulk density. The color of the residues during torrefaction changed from brown at a lower temperature to black at a higher temperature. The condensed fraction was brown liquid mixing water with tar.

The important thermal decomposition reactions during torrefaction of the biomass are dehydration, decarboxylation and deacetylation of the xylan-containing hemicellulose polymers [16]. At low temperature the dehydration known as char-forming reactions predominates and produces volatiles and char. As temperature increases, the depolymerization with production of levoglucosan dominates [22]. The main changes in biomass due to torrefaction involve decomposition of hemicellulose, partial depolymerization of lignin and cellulose (shortening of cellulose macro-fibrils) [17]. Generally, the hemicellulose breaks down firstly at the temperatures ranging from 200 °C to 250 °C, and then does cellulose at the temperatures ranging from 240 °C to 350 °C, with lignin being the last component to decompose at temperatures between 280 °C and 500 °C. Water is a major product released in two different mechanisms, firstly during drying when moisture evaporates and secondly during dehydration reactions between organic molecules. The experiments on the individual components of biomass showed that the cellulose particles shrink slightly as they are heated and charred. Unlike cellulose, particles of pectin and xylan show evidences of softening or melting (at the temperatures of 150 °C and 200 °C, respectively), as well as bubble formation as they are heated. The bubbles are formed within the particles, and as the bubbles burst volatile products are released into the gas stream [26]. The torrefied sample lost most moisture and low weight organic volatile components and then the long polysaccharide chains were depolymerized, thus forming a hydrophobic bio-char with a higher energy density than the raw biomass. The heating value of the torrefied residues are also shown in Table 2. The value compared with the raw material increases by 17% for the rice straw and 15% for the rape stalk, respectively at the temperature of 300 °C.

Fig. 1 shows the comparison of conversion between agricultural residues and woody biomass from literatures. The conversion of the agricultural residues is higher than that of the latter under the same torrefaction conditions (temperature and residence time), especially 40% more at 250 °C. This is due to the higher volatile matter content in the agricultural residues and the decomposition of hemicellulose, the main fraction decomposed in the temperature range of torrefaction [27].

3.2. Grindability of solid bio-char

The torrefied biomass is more brittle with much better milling properties [17]. Fig. 2 shows the pulverized particle size distributions of the torrefied agricultural residues and the original biomass. It can be observed that the ratio of coarse particle size decreases sharply for both kinds of samples after torrefaction. The top areas, 70% and 69%, respectively, represent particles with size

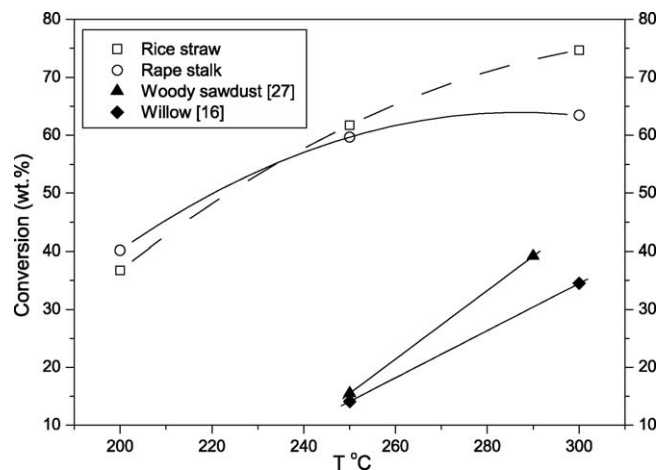


Fig. 1. Conversion of the rice straw and rape stalk. Comparison with woody biomass in Refs. [16,27].

of more than 450 µm in the original materials in the first two columns. The data states the difficulties encountered in grinding the agricultural biomass. However, the percentage of fine particles increases with the increase of the torrefaction temperature. It indicates that 97% of the pulverized torrefied rice straw passes through the sieve with mesh sized 450 µm at the case of 250 °C, while, 84% for the rape stalk. Comparatively, the rice straw has a higher grindability than the rape stalk after torrefaction. Extra moisture is a factor affecting further grinding of the biomass [22]. The decomposition reactions at such low temperature level cause the biomass to become completely dried and to lose its tenacious and fibrous structure. Therefore, the grindability of the biomass is improved significantly. However, it is noted that the slim powder of biomass is different from the coal particles which generally have spherical or cubic shapes. As a result, the particle diameter (shortest dimension) of the torrefied biomass is so small that the particle can be sieved, while the length dimension of the particle is larger than the sieve opening.

Both the torrefaction process at higher temperature and pulverization to lower size will increase the energy consumption, though the biomass fuel is improved in properties and reactivity. In the literatures [6,17], the recommended torrefaction temperatures for wood are 240 °C, 270–280 °C and holding time about 0.5 h. The energy loss in the production of torrefied agricultural residues is moderately higher than that of woody biomass so that the torrefaction temperature of 250 °C and residence time of 0.5 h is to be suitable.

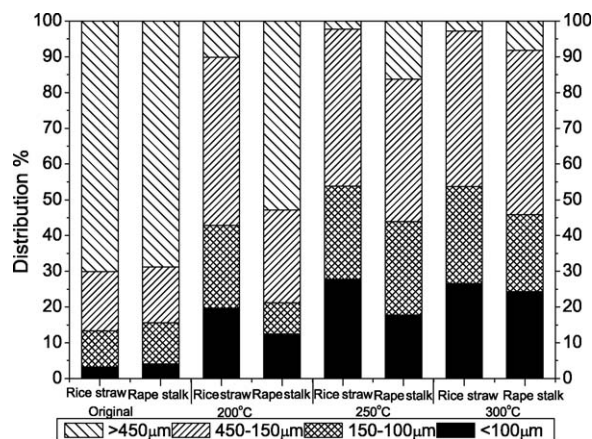


Fig. 2. Particle size distribution of the ground samples wt%.

3.3. Gas products

The gaseous products were carbon dioxide, carbon monoxide and methane, since the methane arises from the cracking and depolymerization reactions, and oxides of carbon, CO and CO₂, from decarboxylation and depolymerization [5]. At low temperature the pyrolysis gas mainly consists of CO₂ (the largest contribution 85–74%), CO (15–20%), lower amounts of CH₄ (1%), negligible H₂ and

hydrocarbons. According to the literature [28], the production of hydrogen during pyrolysis is negligible for most biomass when temperature is below 530 °C because this gas is mainly caused by the decomposing of volatile matter. A comparison between wood and agricultural residues in gas composition indicates that the latter is characterized by a higher CO₂ production.

The yields of all gas components increase with the reaction temperature increasing, as presented in Fig. 3(a–f). For the rice

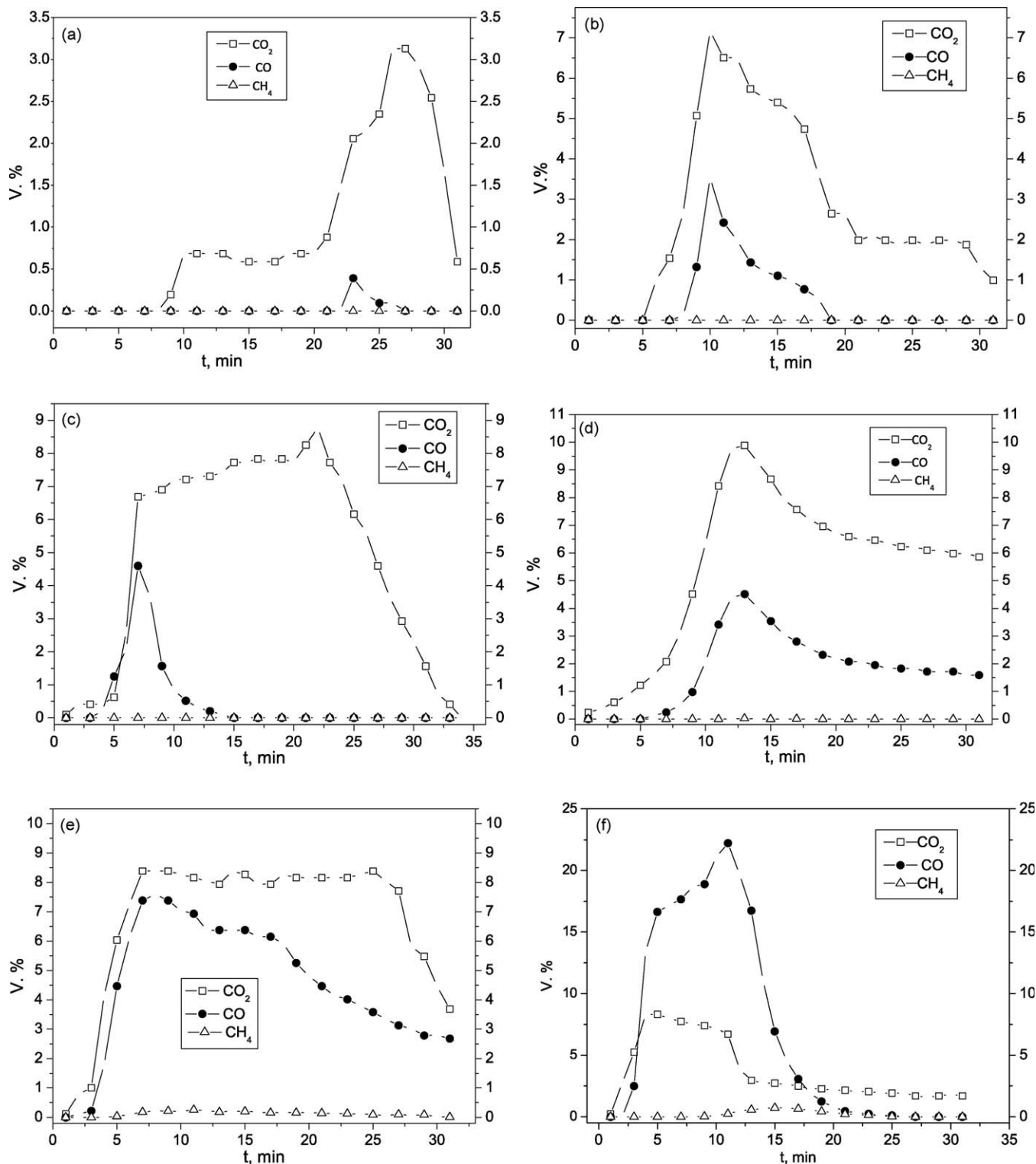


Fig. 3. CO₂, CO and CH₄ yields of the torrefied rice straw and rape stalk as functions of residence time and temperature. Rice straw at (a) 200 °C, (b) 250 °C, and (c) 300 °C; rape stalk at (d) 200 °C, (e) 250 °C, and (f) 300 °C.

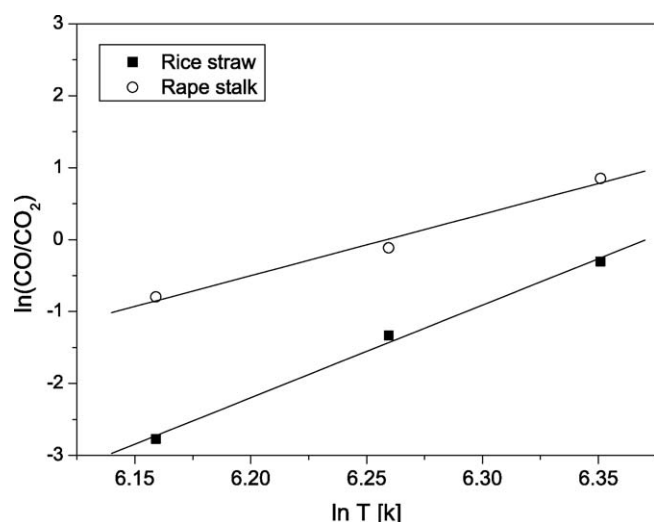


Fig. 4. Logarithm of the ratio CO/CO₂ yields to the logarithm of temperature for the rice straw and rape stalk.

straw, the gases begin to be generated after nearly 7 min heating at 200 °C although this period is shorter at higher temperature. This may be explained by the high moisture content (up to 5.12%) in the rice straw. After half an hour, the torrefaction is almost finished and the emission of CO is completed earlier than CO₂. The methane was not detected because the value was lower than 0.001%. Nevertheless, for the rape stalk, the gases are released upon the temperature attaining 200 °C. The decomposition processes are still generating gases after 30 min heating while the concentrations of all gases have decreased sharply. In the case of 300 °C, this process only lasts for 20 min and then little gas is detected.

Pyrolysis studies report general approximate relationships among the ratios of the major gas products, CO, CO₂ and CH₄, over wide ranges of experimental conditions. These are due to comparable values of the activation energies for the formation of different species [28]. Fig. 4 is a plot illustrating the logarithm of the yield ratio of major gas species CO/CO₂. A linear dependence is roughly established for the two samples. It is indicated that the major gas species present comparable kinetic constants also for torrefaction process. The ratio increases with the increasing temperature because some parts of cellulose and lignin may decompose at higher temperature. At temperature below 220 °C, cellulose loses weight mainly due to the formation of water, but at temperature of up to 250 °C, CO₂ and CO also evolve [15]. Moreover, the line of the rice straw is under that of the rape stalk because the former has a lower yield of CO and a higher yield of CO₂, probably as a result of the higher cellulose content.

3.4. Kinetic model of gas generation

The models used here are normally based on the mechanisms involving series-parallel reactions. The generation of gases during torrefaction is assumed to be a series of independent first-order parallel reactions, each having individual apparent activation energy. The references [5,29] gave the details on the kinetic study of gas generation. A similar approach is applied in the generation of gases during low temperature torrefaction. Eq. (1) describes the change of gas moles with the time.

$$\ln\left(\frac{M_0}{M_0 - M}\right) = k \cdot t \quad (1)$$

where M , k represent the number of gas moles generated at given time t and the rate constant of gas formation, respectively.

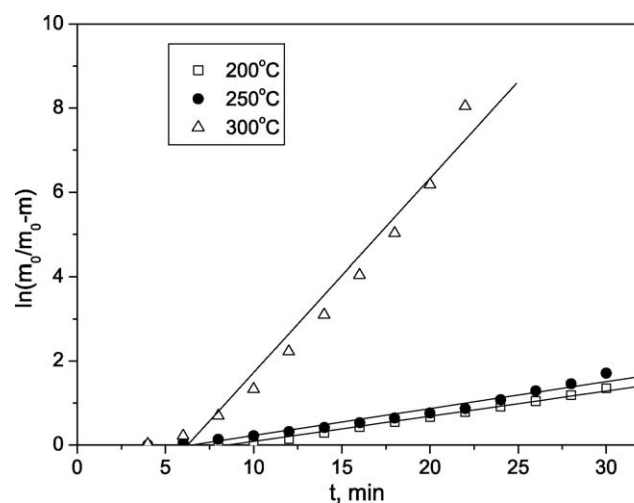


Fig. 5. Verification of Eq. (1) for the kinetic model of CO. Torrefaction of the rape stalk.

And M_0 represents the total moles of gas generated during the whole torrefaction process of biomass. This value is obtained from the experiments carried out at a relatively long time until the concentration of the gases is nearly zero.

A plot of the left-hand side of Eq. (1) vs. time should yield a straight line with a slope of k . The values of k were obtained from the least-squares fit of the experimental data. Fig. 5 shows a plot of Eq. (1) for the carbon monoxide in the experiments of the rape stalk at different temperatures. The rate constants for all gases in the experiments are presented in Table 3, with values of $R^2 = 0.97$ –0.99

Table 3

Rate constants of the three gases formation in the torrefaction of the two agricultural residues.

Sample	Temperature (°C)	$k \times 10^3 \text{ min}^{-1}$		
		CO	CO ₂	CH ₄
Rice straw	200	454.62	74.1	n.a. ^a
	250	519.32	166.07	n.a.
	300	730.43	214.49	n.a.
Rape stalk	200	59.86	13.17	8.17
	250	64.06	21.07	104.6
	300	460.62	33.21	428.9

^a n.a.: not analyzed.

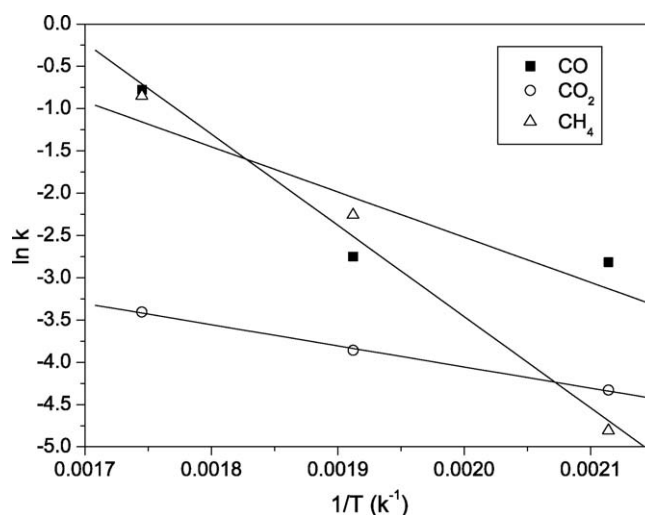
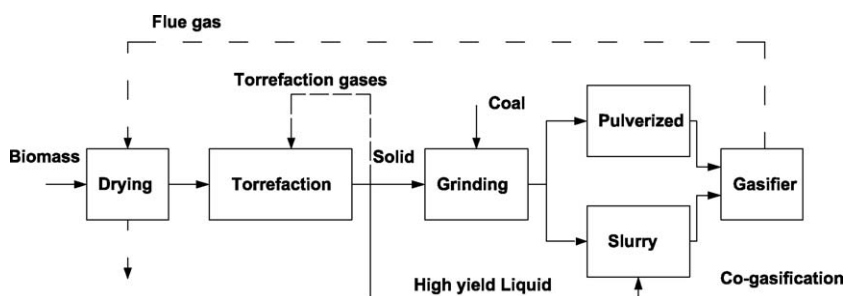


Fig. 6. Arrhenius plot for gases formation in the torrefaction of the rape stalk.

Table 4Activation energy and Arrhenius pre-exponential factors of CO, CO₂ and CH₄ formation in the torrefaction of agricultural residues.

Sample	Gas	Activation energy (E_a) (kJ mol ⁻¹)	Pre-exponential factor (k_0) (min ⁻¹)	Correlation coefficient (R^2)
Rice straw	CO	10.5	6.3	0.95
	CO ₂	24.3	37.9	0.97
Rape stalk	CO	44.5	3564.6	0.85
	CO ₂	20.8	2.57	0.99
	CH ₄	89.7	7.5×10^7	0.99

**Fig. 7.** Basic principle concept for autothermal torrefaction integrated with coal co-gasification.

for the rape stalk and 0.89 to 0.98 for the rice straw, respectively. The value of k increases with the increasing temperature for all gases, though the magnitude is small for CO₂.

Thus, from the values of rate constants of different temperatures, the activation energies for the formation of each gas can be obtained by means of an Arrhenius function Eq. (2). Fig. 6 shows the Arrhenius plots for CO, CO₂ and CH₄ formation during the rape stalk degradation. With temperature increasing, an increase in kinetic constant is observed. Carbon monoxide and methane present a faster increase than carbon dioxide, which is coincident with the literature [29].

$$\ln k = \ln k_0 - \frac{E_a}{R} \cdot \frac{1}{T} \quad (2)$$

Table 4 shows the activation energies and the Arrhenius pre-exponential factors for the formation of main gases and correlation coefficients of the least-squares analysis. It can be observed that the activation energies for the formation of CO₂ are independent of the type of residue, but those for CO are remarkably different from the types of the raw materials. Additionally, the activation energy of CH₄ formation in the torrefaction of the rice straw is not available because of the negligible concentration at low temperatures.

3.5. Torrefaction combined with co-gasification

The torrefied agricultural residues may be suitable for gasification in coal gasifier. During torrefaction, the biomass loses relatively more oxygen and hydrogen compared to carbon. The low ratio of O/C can improve the gasification properties of the torrefied biomass compared to the raw material [16]. The net calorific value of the torrefied biomass increases. The moisture content of the torrefied biomass is very limited because of dehydration reactions [30]. The torrefied biomass becomes more porous and more fragile because it loses its mechanical strength as mentioned in Section 3.2. Inherent high content of inorganic matter may act as catalyst and improve the efficiency of gasification. The low temperatures of the devolatilization stage allow the alkali metals to be retained in the solid phase product [31,32]. Alkali metals such as potassium are known to be active catalysts for gasification of bio-char [33]. On the other hand, the torrefaction process is a slightly endothermic

process requiring approximately 0.6–1 MJ kg⁻¹ based on an energetic balance of the overall process and products in HHV terms [17]. A method combined wood torrefaction with CFB gasification has been established by Prins [16]. But the author advised that oxygen-blown entrained flow gasification of torrefied wood seemed to be an attractive option to conserve the chemical exergy of wood in the product gas maximally because of high gasification temperature.

An optional system for coal co-gasification in entrained flow gasifier with torrefied agricultural biomass is shown in Fig. 7. There are several advantages for this combined system. Firstly, the small pretreatment factories of torrefaction can be built near the resources, which produce a higher energy content and convenient char or gases for the large scale gasifier far away from farmland. The torrefied biomass can be milled together with coal in the mill. The high liquid yields from some crop straw may be mixed directly with the coal slurry. Secondly, the gases from torrefaction can supply energy by directly or indirectly heating the pyrolysis reactor. Thirdly, the raw biomass always contains some moisture which causes the efficiency of gasifier decreasing by 1.5 percent points when the moisture content increases from 0.7% to 8.6% [16]. Finally, the entrained flow gasifier almost operates at elevated pressure, which is beneficial for many subsequent processes such as gas turbines and chemical synthesis. In comparison, the biomass gasifier often operates at atmosphere due to the difficult feeding of bulk biomass.

4. Conclusions

The torrefaction has a great effect on the physical and chemical properties of the torrefied agricultural residues. The main conclusions of this work are:

- (1) The solid yield decreased rapidly during torrefaction when the temperature increased, but the heating value of the torrefied residues increased. The conversion rate of agricultural residues is higher than that of woody biomass. This is because of a higher hemicellulose content in the herbaceous biomass which is more reactive under torrefaction temperature level. The bio-chars from the rape stalk (except for 200 °C) were less than that of the rice straw as a result of high volatile matter content which produced more liquid and gases during torrefaction.

- (2) The grindability of the torrefied agricultural residues is greatly improved with increasing temperature. Under the same conditions, only 30% of particles from ground raw materials can pass through the sieve with mesh sized 450 μm , however, 90% and 50% for the torrefied rice straw and rape stalk, respectively.
- (3) The gas composition mainly consisted of CO_2 , CO and little amounts of CH_4 . The gases generation of the rice straw is put off for several minutes due to the high moisture content. The ratio of CO to CO_2 was increasing with the increase of temperature because some cellulose and lignin were decomposed at higher temperature. By kinetic study, it was concluded that three main gases, CO_2 , CO and CH_4 , were formed by parallel independent first-order reactions.
- (4) The torrefied agricultural residues have favorable properties, such as very low moisture content, high energy density, tendency to pulverize, that are very similar to that of coal. Therefore, the torrefaction process is a promising pretreatment method for agricultural residues to combine with coal co-gasification.

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